Refractometer Cell for both Absolute and Differential Refractive Index Measurement of Fluids

Background

The difference in refractive index between a sample and a reference material is called the differential refractive index, or DRI, and is a physical parameter of considerable importance. In liquid chromatography, the DRI between a sample liquid consisting of a mobile phase plus a solute and a reference liquid, which is the pure mobile phase, is often used as a determination of solute concentration. Another physical parameter of interest is the absolute refractive index, RI, of a fluid. In general chemistry, the RI is used to identify liquids, determine the purity of liquids, and to measure high concentrations of dissolved molecules such as sugar solutions. In light scattering measurements, the RI of the mobile phase is an important input parameter in determining the molar mass and size of molecules and particles.

To date there has been no one instrument which can measure both the DRI between a sample fluid and a reference fluid, and the RI of a fluid. A typical instrument for measuring the DRI only is a "walk-off" type differential refractometer. That instrument contains a transparent cell containing two fluid chambers, and having an angled transparent window separating the chambers. A beam of light passes into the cell, through one chamber, through the angled window separating the chambers, through the second chamber, and finally out of the cell, as pictured in Fig. 1. For the cell pictured, if the fluids in the two chambers have identical indices of refraction, then after exiting the cell, the transmitted beam of light travels in a path parallel to the incident beam. If the two fluids have different indices of refraction, then the transmitted beam of light travels at an angle different from the direction of the incident beam. The angle between the

1   incident light beam and the transmitted light beam is, to first order, proportional to the difference

2   in refractive index between the two liquids. The angular deflection of the light beam may be

3   measured by a variety of well-established techniques, and so the DRI of one fluid relative to the

4   other may be measured and reported. It is noted that the fluids are usually introduced into the

5   respective chambers by connection means providing flows transverse to the planes shown. Each

6   chamber contains means to introduce and remove fluids contained therein, usually on opposite

7   sides of the chambers.

8   A very simple, though imprecise, instrument that may be used for the measurement of the

9   RI of a fluid is comprised of a transparent cell with only one fluid chamber. The fluid chamber

10   has at least one wall that is oriented with respect to the incoming beam, as shown in Fig. 2. A

11   beam of light passes into the cell, through the fluid, and exits the cell via the angled face. The

12   transmitted beam will have an angular deflection that depends upon the index of refraction of the

13   fluid relative to the known RI of the air or medium surrounding the cell. Embodiments that are

14   more precise would include the well-known Abbe refractometer. As with the DRI instrument,

15   that angular deflection may be measured by a variety of well-established techniques, and so the

16   RI of the fluid may be reported. Note that the chambers used in the structures of Figs. 1 and 2

17   are defined generally in terms of right triangles.

18

19   **Brief description of the invention**

20   This invention allows one instrument to measure separately the RI of a sample fluid and the DRI

21   between a sample fluid and a reference fluid. The invention is comprised of a new type of flow

22   cell that contains two chambers, typical of a DRI instrument, but an asymmetric internal angle in

23   either the sample or the reference chamber. By the provision of this unique structure, it is an

1   objective of this invention to be able to measure the refractive index of a fluid relative to the

2   refractive index of the material comprising the flow cell or relative to the medium surrounding

3   the flow cell, either of which may be considered a measurement of the RI of the fluid. In general,

4   the preferred embodiment of the flow cell of the invention would be surrounded by air. An

5   additional objective of the invention is to be able to measure the difference in refractive index of

6   a sample fluid relative to that of a reference fluid. With the addition of mirror means, it is the

7   further objective of this invention to improve its sensitivity. Another objective of this invention

8   is to measure precisely the refractive index of the fluid-containing cells using well-characterized

9   reference fluids. A further objective of the invention is to measure the asymmetric internal angle

10   of the flow cell using well-characterized reference fluids.

11

12   **Brief description of the figures**

13   Figure 1 illustrates a typical differential refractometer cell.

14   Figure 2 illustrates an absolute refractometer cell.

15   Figure 3 illustrates the preferred embodiment of the inventive cell including an asymmetric internal

16   angle in one of its chambers.

17   Figure 4 illustrates the preferred embodiment of the invention whereby a reflective means has

18   been added to the cell of Fig. 3.

19

20   **Detailed description of the invention**

21   For a typical DRI cell, as that pictured in Fig.1, if chambers **4** and **5** are filled with

22   identical fluids, $n_1 = n_2$, the transmitted light beam **2** leaves the cell parallel to the direction of the

23   incident beam **1**. Note that the preferred embodiment of such DRI cells require that the fluid

1   containing chambers **4** and **5** are similar triangles of right angle structure with their hypotenuses

2   parallel to each other and their light transmitting sides parallel both to each other and to the

3   external cell surfaces. When $n_1 \neq n_2$, the transmitted beam **3** now exits at some angle θ to the

4   direction of the incident beam. In a simple absolute refractometer, as shown in Fig. 2, the light

5   beam **1** is refracted as it passes through the sample chamber **4**, thus emerging **3** at an angle ϕ.

6   A preferred embodiment of the invention is shown in Fig. 3 wherein chamber **6** is no

7   longer a right triangle, *i. e.* the surface **13** is not parallel to surface **10**. Unlike the traditional

8   configuration of Fig. 1 where both chambers form right triangles, the second chamber cavity is

9   not a right triangle. For the case that both chambers are filled with the same liquid, *i. e.* $n_1 = n_2$,

10   the incident light beam **1** deflected by an angle ϕ which is a function of the refractive index

11   difference between the fluid n_2 in chamber **6**, the refractive index of the material comprising the

12   cell, and the angular deviation of plane **13** from parallelity with plane **10**. In general, the

13   preferred embodiment of such chambers would be directed to structures surrounded by air.

14   Theoretically, the surrounding media might be different than air, in which case the deflection

15   angle measured would depend also upon the RI of the medium surrounding the cell. As such

16   cases are easily represented by relations similar to those to be derived herewith, it will be

17   assumed that the surrounding RI is equal to that of air, *i. e.* 1.0. Changing the RI of the

18   surrounding medium is but an obvious variation of the simpler case of air discussed here. When

19    $n_1 \neq n_2$, the incident light beam **1** is deflected by an additional angle θ which is a function of the

20   difference in refractive index between the fluid n_1 in chamber **4** and the fluid n_2 in chamber **6**.

21   Thus the light beam **8** exits the cell at some angle $\phi + \theta$. That additional angle θ becomes a

22   measure of the DRI between n_1 and n_2.

1   The succesive surfaces through which the light beam passes are labeled in Fig. 3 as

2   planes **9, 10, 11, 12, 13,** and **14.** As discussed above, an angular deviation ϕ due to the

3   refractive index difference between a fluid in chamber **4** or **6** and the material comprising the cell

4   results from nonparallelism of planes **10** and **13.** If, as is shown in Fig. 3, planes **9, 10,** and **14**

5   are parallel to each other, but are not parallel to plane **13,** then the angular deviation ϕ is due to

6   the refractive index difference between a fluid in chamber **6** and the material comprising the cell.

7   For the case of $n_1 = n_2$, by measuring the angular deviation ϕ and knowing the refractive index of

8   the material comprising the cell, we may report the RI of the identical fluids in chambers **4** and

9   **6.** If planes **9** and **10** are parallel to each other and planes **13** and **14** are parallel to each other,

10   but planes **9** and **10** are not parallel to planes **13** and **14,** then the angular deviation ϕ is due to

11   the refractive index difference between the identical fluids and the surrounding medium,

12   typically air. For the case of $n_1 = n_2$, by measuring the angular deviation ϕ and knowing the

13   refractive index of the medium surrounding the cell, typically air, we may report the RI of the

14   identical fluids in chambers **4** and **6.** Planes **11** and **12** are, in the preferred embodiment of this

15   invention, always parallel as is the case for the conventional deflection type of DRI detector.

16   The DRI cell pictured in Fig. 1 and the invention pictured in Fig. 3 show, for purposes of

17   clarity, a light beam traversing the cell only once. In fact, most DRI instruments incorporate a

18   mirror **15** as shown in Fig. 4 placed some distance behind the cell, causing the light beam to

19   traverse the cell twice, thus doubling the angular deflection for a given DRI. Such mirrors will

20   also double the angular deflection for a given RI. Fig. 4 shows the preferred embodiment of the

21   invention with a light beam traversing the cell twice. In addition, angles of importance, α and β,

22   have been labeled for further discussion and explanation in this description. Chamber **4** contains

1   a fluid with index of refraction n_1, chamber **6** contains a fluid with index of refraction n_2, the cell

2   material has index of refraction n_g, and the medium surrounding the cell has index of refraction

3   n_0. Chamber **4** is an isosceles right triangle of base angle α. Chamber **6** has angles α, $\beta < \alpha$,

4   and $\pi - \beta - \alpha$. As in Fig. 3, planes **9**, **10**, and **14** are parallel to each other and are not parallel to

5   plane **13**, and planes **11** and **12** are parallel to each other. The light beam **16** exits at an angle ψ

6   with respect to the incoming beam **1**. For the special case of $\alpha = \dfrac{\pi}{4}$ the angle of the outgoing

7   beam **16** may be found to be, with the RI of the surrounding medium given by n_0,

8

$$\sin(\psi) = \frac{n_1\sqrt{2}}{n_0 2} \left\{ \left[1 - \left(\frac{n_2}{n_1}\right)^2 \left(\sin^2(\beta)(1 - \left(\frac{n_g}{n_2}\right)^2 f^2) - 2\sin(\beta)\cos(\beta)\left(\frac{n_g}{n_2}\right)f\left(1 - \left(\frac{n_g}{n_2}\right)^2 f^2\right)^{\frac{1}{2}} + \cos^2(\beta)\left(\frac{n_g}{n_2}\right)^2 f^2 \right) \right]^{\frac{1}{2}} \right.$$

$$\left. - \left(\frac{n_2}{n_1}\right) \left[\sin(\beta)\left(1 - \left(\frac{n_g}{n_2}\right)^2 f^2\right)^{\frac{1}{2}} - \cos(\beta)\left(\frac{n_g}{n_2}\right)f \right] \right\}$$

9   (1)

10   with

11   $f = \sin(2\beta)g - \cos(2\beta)\left(1 - g^2\right)^{\frac{1}{2}}$

12   and

13   $g = \left(\frac{n_2}{n_g}\right)\left\{ \cos(\beta)\frac{n_1\sqrt{2}}{n_2 2} - \sin(\beta)\left[1 - \left(\frac{n_1}{n_2}\right)^2 \frac{1}{2} \right]^{\frac{1}{2}} \right\}.$

14

1   The angle β may be determined directly from measurement of the deflection angle ψ after filling

2   both chambers with the same fluid whose refractive index n_1 is known at the wavelength λ_0 of

3   the incident light beam. In this event, setting $n_1 = n_2$, Eq. (1) simplifies to

$$\sin(\psi) = \frac{n_1\sqrt{2}}{2}\left\{\left[1-\left(\sin^2(\beta)(1-\left(\frac{n_g}{n_1}\right)^2 f^2)-2\sin(\beta)\cos(\beta)\left(\frac{n_g}{n_1}\right)f\left(1-\left(\frac{n_g}{n_1}\right)^2 f^2\right)^{\frac{1}{2}}+\cos^2(\beta)\left(\frac{n_g}{n_1}\right)^2 f^2\right)\right]^{\frac{1}{2}}\right.$$

4    $$\left.-\left(\frac{n_2}{n_1}\right)\left[\sin(\beta)\left(1-\left(\frac{n_g}{n_1}\right)^2 f^2\right)^{\frac{1}{2}}-\cos(\beta)\left(\frac{n_g}{n_1}\right)f\right]\right\}$$

5   (2)

6   where $g = \left(\frac{n_1}{n_g}\right)\{\cos(\beta)-\sin(\beta)\}\frac{\sqrt{2}}{2}$.

7

8   In the event the cell refractive index n_g is also unknown, it is easily determined by using two

9   reference fluids whose two corresponding refractive indices are n_1 and n_2, respectively. In this

10   event, one fills both chambers first with the solution of known refractive index n_1 and then

11   measures deflection angle ψ per Eq. (2). Next one fills both chambers with the solution of known

12   refractive index n_2 and then measures the new deflection angle ψ' per Eq. (2), with n_1 replaced

13   by n_2 and ψ' by ψ'. The two unknowns β and n_g may then be determined from the relations of

14   Eq. (2) and the two aforementioned measurements.

15

1   Assuming a reference fluid in chamber **6** and a sample fluid in chamber **4**, we may expand Eq. 1

2   making the substitution $n_1 = n_2 + \Delta n$. Assuming also that $n_0 = 1$, then to first order in $\beta - \dfrac{\pi}{4}$

3   and to second order in Δn, Eq. (1) may be written as:

4

5    $$\sin(\psi) = 2\Delta n\left\{1 + \left(1 - \frac{n_g}{n_2}\right)\left(\beta - \frac{\pi}{4}\right)\right\} + 2(n_g - n_2)\left(\beta - \frac{\pi}{4}\right) + \Delta n^2\left\{\left(11\frac{n_g}{n_2^2} - \frac{1}{n_g} - \frac{10}{n_2}\right)\left(\beta - \frac{\pi}{4}\right) - \frac{1}{n_2}\right\}$$

6   (3).

7

8   For $\Delta n = 0$ (same fluid in both the sample and reference cells) the angle ψ of the outgoing

9   beam **16** is proportional to the difference between the indices of the fluid, n_2, and the cell

10   material, n_g, with a proportionality constant of $2\left(\beta - \dfrac{\pi}{4}\right)$. If the index n_g and angle β are

11   known, then by measuring $\sin(\psi)$ we may calculate n_2, the absolute refractive index of the fluid.

12   If the cell material refractive index n_g and angle β are unknown, and at least two different fluids

13   are available with known refractive indices, then as described above, by measuring $\sin(\psi)$ as a

14   function of $n_1 = n_2 = n$, we may determine experimentally the cell material refractive index

15   n_g and angle β. For a given n_2 we then may change the index of refraction of the sample fluid

16   producing a nonzero Δn. The outgoing beam will have a change in $\sin(\psi)$ which is to first order

17   proportional to Δn. Finally, by measuring the change in $\sin(\psi)$, we may calculate Δn.

18   It is not necessary for the reference liquid to be contained in chamber **6**. If instead of

19   assuming that chamber **6** contains the reference fluid, we assume that chamber **4** contains the

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1   reference fluid, we may expand Eq. (1) making the substitution $n_2 = n_1 + \Delta n$. Assuming $n_0 = 1$,

2   to first order in $\beta - \dfrac{\pi}{4}$ and to second order in Δn, Eq. (1) becomes:

3     $\sin(\psi) = -2\Delta n\left\{1+\left(1-\dfrac{n_g}{n_1}\right)\left(\beta-\dfrac{\pi}{4}\right)\right\} + 2(n_g - n_1)\left(\beta - \dfrac{\pi}{4}\right) - \Delta n^2\left\{\left(-9\dfrac{n_g}{n_1^2}+\dfrac{1}{n_g}+\dfrac{10}{n_1}\right)\left(\beta-\dfrac{\pi}{4}\right)+\dfrac{1}{n_1}\right\}$

4   (4).

5

6   As with the previous expansion, the DRI and RI for the fluids may be separately determined, or

7   with at least two fluids of known refractive index, we may determine the cell material refractive

8   index n_g and angle β.

9   Equation (1) and its subsequent expansions are based upon the specific geometry of

10   Fig. 4. It will be clear to those skilled in the art of refractometry that the dRI and fluid RI may be·

11   determined separately for any case of nonparallelism of planes 10 and 13, and/or planes 11 and

12   12. It will be clear also to those skilled in the art of refractometry that by varying the angles of

13   the external planes 9 and 14 it is possible to reference the RI of the fluid to the refractive index of

14   the material comprising the cell, or to the refractive index of the medium surrouding the cell. As

15   long as at least one of the plane pairs 10 and 13 or 11 and 12 are not parallel, the cell may be

16   used to determine both the RI of an unknown fluid as well as the DRI between two different

17   fluids such as a solvent and a solution in which a solute is dissolved in the solvent. Obviously, if

18   more than a single plane of each of the afore-referenced pairs is not parallel, that type of cell will

19   also represent also another embodiment of my invention. For the case of such additional non-

20   parallel surfaces, it must be emphasized that more generalized relations than indicated by Eq. (1)

21   *et seq.* are easily derived. The associated internal angles of each such surface must be known or

1   determined before my invention be applied. This will require a plurality of fluids whose RI

2   values are known to derive these angles by refraction measurements such as described herein.

3   Key to the RI determinations that may be achieved by the preferred embodiment of the

4   inventive methods described herewith is the solution of Eq. (1) for the variety of conditions that

5   may be appropriate to the desire of the instrument user. For the practical ranges of the refractive

6   indices of sample and reference fluids, the approximations of Eq. (3) or Eq. (4) will suffice to

7   yield the RI of unknown fluids and/or the DRI of a sample fluid relative to a reference fluid to

8   sufficient precision for both chromatographic and stand-alone purposes. In the event that

9   additional precision is required, it become a simple task to solve Eq. (1) directly by, for example,

10   Newton's method using the approximations of Eq. (3) or Eq. (4) as a starting point.

11

12   In the description of the multifunction refractometer that I have discussed above, I have

13   emphasized the numerous variations on my invention that will be clearly obvious to those skilled

14   in the art of refractometry. Such variations are but obvious extentions of the invention I claim as

15   follows: